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(54) Title: SUBSTRATES FOR SUPERCONDUCTORS

100	
101	SELECT AND WEIGH THE CONSTITUENT METALS
102	MELT THE CONSTITUENTS AND COOL
103	REMELT TO ENHANCE HOMOGENEITY
104	SHAPE THE SOLIDIFIED MELT AND REDUCE IN SIZE TO FURTHER HOMOGENIZE
105	MECHANICALLY DEFORM THE SHAPE TO A SMALLER SIZE AND RECRYSTALLIZE TO FORM A SMALL GRAIN SIZE
106	DEFORMING THE SHAPE IN AN AXIALLY SYMMETRIC MANNER TO A SMALLER SIZE.
107	PLANAR DEFORM THE ALLOY TO A REDUCTION IN THICKNESS OF BETWEEN 85% TO 99.9%
108	HEAT TREAT AT A TEMPERATURE EXCEEDING 250°C BUT NOT MORE THAN 85% OF THE MELTING TEMPERATURE

## (57) Abstract

An alloy capable of forming a (100) [001] cube-texture by thermo-mechanical techniques has 5-45 atomic percent nickel with the balance being copper. The alloy is useful as a conductive substrate for superconducting composites where the substrate is coated with a superconducting oxide. A buffer layer can optionally be coated on the substrate to enhance deposition of the superconducting oxide. The method for producing the alloy includes weighing the metal (101), melting and cooling the constituents (102). The alloy is remelted (103) and shaped (104). The alloy is then mechanically deformed to a smaller size and recrystallize (105) then deformed in an axially manner (106) and planar deformation (107). The final step is heat treated (108).

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SUBSTRATES FOR SUPERCONDUCTORS

This invention was made under a Cooperative Research and Development Agreement with Los Alamos  
5 National Research Laboratory. The United States Government has certain rights in this invention.

Background of the Invention

The present invention relates to substrates for superconductors, and more particularly to copper-nickel  
10 substrates for receiving the deposition of YBCO ( $\text{YBa}_2\text{Cu}_3\text{O}_x$ , or Yttrium-Barium-Copper-Oxide) high temperature superconducting layers to form so-called YBCO coated conductors. Other closely related superconducting materials which can be used are  $\text{REBa}_2\text{Cu}_3\text{O}_x$ , in which the Y  
15 has been partially or completely replaced by rare earth (RE) elements.

YBCO ( $\text{Y-Ba}_2\text{-Cu}_3\text{-O}_x$ ) is an important superconducting material for the development of superconducting tapes that can be used in superconducting transmission cables,  
20 superconducting current leads, superconducting coils for transformers, superconducting magnets for AC and DC motor applications, and superconducting current limiters, as well as other electrical conductors. These applications are based on a basic property of a superconducting  
25 material: it has no electrical resistance when cooled below its transition temperature, and can carry a DC electric current without power dissipation.

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For the production of YBCO coated conductors, thin substrate tapes (or foils) are typically coated with a thin buffer layer, which in turn is coated with a YBCO layer. A suitable heat treatment is then performed to  
5 optimize the superconducting properties of the YBCO layer. One of the functions of the substrate is to impart mechanical strength to the resulting superconducting tape. A second function, which depends on the process type, is to act as a template for a well-  
10 textured buffer layer. Compared to the substrate material, this buffer layer provides a much better deposition surface for the YBCO layer in terms of lattice match, texture, coefficient of thermal expansion (CTE) and chemical compatibility. To obtain good  
15 superconducting properties, the buffer layer needs to be bi-axially textured - meaning that a lattice plane, preferably its cubic (or tetragonal) lattice face, is oriented such that the cube face is parallel to the tape surface in a substantial majority of its crystallites.  
20 In addition, the cube edge in each crystallite should be parallel to the cube edges in all neighboring crystallites.

Some specialized techniques such as Ion Beam Assisted Deposition (IBAD) or Inclined Substrate  
25 Deposition (ISD) can deposit a bi-axially textured buffer layer on top of a random polycrystalline or even amorphous substrate. In general, these deposition

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techniques are very slow or are effective in only a narrow region, and they are not suited for large scale and economical manufacturing of YBCO coated conductors. A more advantageous method is the epitaxial deposition of a bi-axially textured buffer layer (or YBCO superconducting layer) on top of a bi-axially textured metallic substrate. Examples of epitaxial growth by vapor deposition, electro-plating, or oxidation, in which native oxide layers grow on parent metals, are numerous and well known, as is the fact that many metals can form bi-axial textures. Few of these textures are useful for deposition of buffer layers and YBCO superconducting layers because of misorientation. However, in many rolled, face-centered cubic (fcc) metals, when properly rolled and heat treated, a well-developed, and very useful, cube texture is obtained. The cube faces are parallel to the rolled surface and a cube edge typically points in the same direction as the rolling direction. Such a texture is called a cube-on-cube texture, with a crystallographic notation of (100)[001]. Another well-known cube texture is the so-called Goss texture (100)[011]. These bi-axial textures are part of a larger family called sheet textures. In the following description of the invention the (100)[001] texture will be referred to as the "cube" texture.

To deposit the buffer layer in an epitaxial manner on the substrate, the substrate material needs to meet

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certain requirements. The substrate must have a lattice constant and a CTE which are compatible with the buffer layer material and also with the YBCO layer. Ideally, the substrate will yield a bi-axial texture by simple  
5 thermo-mechanical means. The substrate is preferably non-magnetic at cryogenic temperatures, that is, at temperatures between room temperature and that of liquid helium, or 4.2 degrees Kelvin. The substrate must be electrically conductive, relatively strong at room  
10 temperature, and oxidation resistant at elevated temperatures. There are several metals, such as copper or nickel, that can be bi-axially textured by rolling a selected copper or nickel stock, followed by a so-called secondary recrystallization at an elevated temperature.  
15 However, these pure metals have significant drawbacks in that they are either ferromagnetic (Ni) or are easy to oxidize (Cu).

It is known that some binary alloys (a single phase mixture of two metals) can be made into a bi-  
20 axially textured tape as well. One example of a cube texture which has been produced in an alloy is iron-nickel, but this alloy has proven to be ferromagnetic, which is detrimental to the performance of the device in many applications. In addition, copper-nickel alloys  
25 with small quantities of nickel have previously been textured, but those working in the field believed that



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the maximum Ni content in the Cu-Ni alloy should not exceed 4.2 percent nickel.

#### Summary of the Invention

The present invention features bi-axially textured alloys with a face centered cubic structure, of copper-nickel (Cu-Ni) with 5 to 45 atomic % nickel, preferably 10-40% and more preferably 25-35%, for use as substrate materials for superconducting oxides. Preferred superconducting oxides include the Rare Earth Barium Copper Oxides, (RE)BCO, or Yttrium Barium Copper Oxides, YBCO, but also superconducting oxides from the Thallium, Mercury and Bismuth families. The combination of the substrate and the oxide forms a coated conductor. These Cu-Ni alloys are preferably homogenous, but can have some degree of inhomogeneity with localized concentrations of Ni not exceeding 45%, and can be processed by thermomechanical methods to form tapes with a single (100) [001] cube texture. These alloys are non-ferromagnetic and form good substrate materials for subsequent epitaxial buffer layer and superconductor layer deposition, for use in a variety of products.

The enhanced Ni content achieves desirable features in the alloy, such as increased oxidation resistance, decreased CTE, and increased room temperature and high temperature strength. The increased Ni content does not cause ferromagnetism as long as the Ni content does not exceed 42% for applications down to 4.2 degrees

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Kelvin or 45% for applications at temperatures between 4.2 and 77 degrees Kelvin. With the appropriate buffer layer material, this substrate will not adversely affect the superconducting properties of the superconducting layer.

Cube-textured alloys of the present invention are formed by creating a homogenous solid solution of the alloying elements. The Cu and Ni constituents are weighed, mixed, and melted together to form a CuNi alloy. The starting materials are preferably at least 99% pure. The melt is then cooled to room temperature. The rate of cooling can be slow or fast, with a rapid quench preferred for giving a fine grain size. The solidified alloy is further homogenized by a heat treatment. The alloy is then processed into tape by mechanical means, such as rolling, after which a suitable heat treatment produces the desired cube texture. An optional recrystallization step after the homogenization and partial deformation of the alloy induces a refined grain size of 5 to 70 micrometers, which obtains a cube texture in the rolled and heat treated tapes.

#### Brief Description of the Drawings

Fig. 1 is a block diagram illustrating the process of forming a cube-textured alloy substrate.

Fig. 2 illustrates a partial cross-sectional view of a superconductor composite formed with a cube-textured alloy substrate.

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Fig. 3 illustrates a partial cross-sectional view of a superconductor composite formed with a cube-textured alloy substrate and a textured buffer layer.

Figs. 3A and 3B illustrate partial cross-sectional views of superconductor composites formed with multiple buffer layers.

Fig. 4 illustrates a partial cross-sectional view of a superconductor composite having both sides coated with a buffer layer and a superconducting layer.

Fig. 5 illustrates a cross-sectional view of a superconductor composite in which the coated layers surround the substrate.

Fig. 6 illustrates a cross-sectional view of a superconductor composite with multiple buffer and superconducting layers.

Figs. 7-10 are pole figures of cube-textured alloys.

#### Description of the Embodiments

The present invention provides an alloy with a cube texture which is formed from a single phase mixture of 5 to 45 atomic percent nickel with the balance being copper. A method for making the alloy is also featured.

The cube texture is often indicated by the crystallographic notation (100) [001] and is typically formed by sheet or tape rolling of a suitable metal or alloy, followed by an appropriate heat treatment. Metals or alloys with a face centered cubic (fcc) structure, and

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which have been processed to display a bi-axial cube texture, have crystallites in which the cube faces are parallel to a tape surface while the cube edges point in the rolling direction. The cube-textured alloys of the present invention are particularly useful as substrate materials for superconducting composites. The resulting tape-like structure includes a cube-textured substrate, on which, for example, a bi-axially textured buffer layer can be deposited using an epitaxial deposition process.

10 Subsequently, a bi-axially textured superconducting layer can be deposited, again using an epitaxial deposition process.

The quality of the bi-axial cube texture determines the effectiveness of the substrate for use in super-conducting composites. The orientation of the cube oriented grains should be within a few degrees of the ideal bi-axial cubic orientation. Grains with an orientation which deviates from the cube texture, should be small in number, preferably well below 15 vol%. The quality of these textures is revealed in their X-ray diffraction pole figures, which show the collective orientations of all crystallites in the irradiated area. Random orientations show no concentration in any direction. Quality textures, on the other hand, show sharp peaks in the pole figures. The sharpness of these peaks is expressed as the Full Width Half Maximum (FWHM) value and is indicative of texture quality. The lower

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the FWHM value, the sharper the peak, and hence, the better the texture. For polycrystalline materials, a FWHM value of well below  $10^\circ$  is desired. Typically, FWHM values on the order of  $4-15^\circ$  are achieved in the

5 substrates of this invention. Higher FWHM values can be acceptable for substrate purposes, in particular if this reduced texture is off-set by advantages in other areas, such as improved oxidation resistance, or better chemical or CTE compatibility. In general, alloy substrates result

10 in FWHM values that are often slightly higher than the FWHM values of similarly treated pure metal constituents. The alloying does, however, lead to advantages as mentioned above, such as a non-magnetic substrate, improved oxidation resistance, and improved CTE.

15 When these substrates are used to form superconducting composites, a buffer layer and superconducting layer can be on one side, both sides, partially, or entirely surround the substrate conductor. The buffer layer can be a metal layer or oxide layer, or

20 combinations of both. Each must provide the needed texture, chemical compatibility, matching lattice constant, and proper CTE match. For example, the buffer layer can be a noble metal or noble metal alloy, an oxide with a cubic structure such as, but not limited to, MgO,

25  $\text{CeO}_2$ ,  $\text{Yb}_2\text{O}_3$ , or yttria-stabilized zirconia ("YSZ"), or any combination of oxides and/or noble metals. The buffer layer, which can include multiple layers, is preferably

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deposited in an epitaxial manner, in which the bi-axial texture of the substrate is transferred onto the buffer layer, or first layer of the buffer layer if multiple buffer layers are employed. In this latter instance, 5 each buffer layer transfers its texture to the next layer until the buffer layer is completed. Finally, the top buffer layer transfers its texture onto the YBCO superconducting layer.

Cube-textured alloys of the present invention are 10 formed by creating a homogenous solid solution of the alloying elements. The Cu and Ni constituents are weighed, mixed, and melted together to form a CuNi alloy. The starting materials are preferably at least 99% pure. The melt is then cooled to room temperature. The rate of 15 cooling can be slow or fast, with a rapid quench preferred for giving a fine grain size. The solidified alloy is further homogenized by a heat treatment. The alloy is then processed into tape by mechanical means, such as rolling, after which a suitable heat treatment 20 produces the desired cube texture. An optional recrystallization step after the homogenization and partial deformation of the alloy induces a refined grain size of 5 to 70 micrometers, which obtains a cube texture in the rolled and heat treated tapes.

25 The binary alloys of the present invention have 5 to 45 atomic percent nickel, preferably 25 to 35%, with the balance being copper. The upper limit of 45 atomic

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percent nickel is established to minimize the risk of developing ferromagnetic properties, which are detrimental to the performance of the device in many applications of the oxide layer. Further, by remaining  
5 below the upper limit, the strong bi-axial cube texture of the alloy is maintained, and the alignment of lattice edges allows the alloy to act as a substrate for superconducting applications.

Referring to Fig. 1, a block diagram illustrates  
10 the process 100 for forming a cube-textured alloy. The cube-textured binary alloys of the present invention are created by first selecting and weighing the constituent metals (Step 101) in a mixture of 5 to 45 atomic percent nickel, preferably 10-40% and more preferably 25 to 35%,  
15 with the balance being copper. This solid solution is then melted (Step 102) by various processes known in the art, such as arc melting, induction melting, plasma torch melting, or melting in an electrical resistance furnace or a furnace heated by gas or coal. Melting temperatures  
20 range from 1100°C to 1250°C. A certain level of homogenization is achieved during the melt process due to convection, mechanical stirring, or stirring induced by the melting techniques such as the induction melter. The melting can be performed in air, under vacuum, or under a  
25 protective inert atmosphere such as nitrogen, argon or helium etc. The melting can be repeated several times to further increase homogenization (Step 103). The melt is

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then cooled with the furnace. The solidified melt is shaped, preferably, into a bar. The bar is reduced in diameter by rod rolling, swaging, drawing or extrusion by a factor of about 1.3 to about 20, preferably about 1.3 to 5, and heat treated to further homogenize the alloy (Step 104). A further mechanical reduction in diameter by similar mechanical means follows, to a size where the planar deformation process will commence (Step 105). Before or at this stage a heat treatment can be applied to recrystallize the alloy and obtain a fine grain size of approximately 5 to 70 micrometers, preferably greater than 10 micrometers and less than 40 micrometers (also Step 105). Alternatively, other methods can be utilized to achieve a fine grain size, such as the rapid solidification of the alloy after melting. An example is the atomization of a melt into an alloy powder, which is subsequently consolidated by (hot) pressing or extrusion into a bar, and which is processed subsequently similar to a cast alloy. The alloy sample is subsequently deformed in an axially symmetric manner, such as extrusion, swaging, drawing, or rod rolling to a smaller size which can be round, square or rectangular (Step 106). In yet another alternate process step, the melt can be cast and rolled. This cast can be further homogenized with a suitable heat treatment, rolled to a thinner size, and recrystallized to induce a fine grain size.



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The alloy is then deformed further by various planar rolling methods known in the art (Step 107), to reduce the thickness of the stock by at least 85% and up to 99.9%. The planar deformation is performed at  
5 temperatures between -200 and 600°C, and preferably at room temperature. A recrystallization anneal (Step 108) at a temperature exceeding 250°C, but not more than 95% of the melting temperature, and preferably at temperatures between 400 and 1190°C, produces the desired single cube  
10 texture (100)[001]. Fig. 7 shows a (111) pole figure, of a Cu-16 at% Ni alloy, which demonstrates a single and high quality (100)[001] cube texture. This alloy is made by extrusion of the homogenized alloy to tape, rolling the tape to a reduction in thickness of 96%, and heat  
15 treating the final tape at 850°C for 4 hours in a protective atmosphere. (See Example 3).

Rolling processes suitable for use with the present invention utilize the following parameters. Rolling is typically performed at room temperature, with  
20 rolling between 0.10m/minute and 100m/minute. The reduction schedule can be a constant reduction per pass, or a constant strain per pass, with reduction steps chosen to be between 5 and 40% per pass. The tape can be lubricated during rolling, or rolled without any  
25 lubricant. Bidirectional rolling is preferred. The tapes can be rolled with large diameter rolls (3.5" to 8" or larger in diameter) or preferably with small diameter

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rolls (0.75" to 2" in diameter) which can be backed up by larger rolls, in a so-called four-high arrangement. Alternatives to the four-high arrangement are cluster and planetary rolling mills.

5 Referring to Fig. 2, a partial cross section of a superconducting composite 200 is shown. To form a superconducting composite 200, the above described substrates 201 of cube-textured alloys have at least one surface 202 coated with a superconducting oxide 203, such  
10 as yttrium-barium-copper-oxide (YBCO) or a rare earth barium copper oxide (REBCO) or mixtures of these. The REBCO's are formed by partial or complete substitution of yttrium (Y) in the YBCO with rare earth elements such as praesodium, neodymium, samarium, europium, gadolinium,  
15 terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, lanthenum, or cerium. The coating of the superconducting oxide 203 is preferably approximately 0.2 to 20 micrometers thick, more preferably 1-20 micrometers thick. The coating is applied by any deposition  
20 technique, such as a non-vacuum solution deposition, electroplating, chemical vapor deposition, or physical vapor deposition techniques, such as sputtering, laser ablation, thermal evaporation, electron beam evaporation. These deposition techniques can require a heat treatment,  
25 such as that disclosed in U.S. Patent No. 5,231,074 issued to Cima et al., fully incorporated herein by

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reference, to form the YBCO in an epitaxial manner, and optimize its superconducting properties.

In the Cima patent, highly-textured superconductor oxide thin films are prepared on substrates, including  
5 lattice matched, non-lattice matched, inert and non-inert materials, by metal organic deposition (MOD). Precursor solution composition, as well as processing temperature and atmosphere are selected to control the presence of a transient liquid phase. Superconductor oxide films  
10 characterized by highly textured morphologies and fully dense, homogeneous microstructures are capable of sustaining critical current densities in excess of  $10^4$  A/cm<sup>2</sup> at 77 degrees K. when prepared on non-lattice matched substrates or critical current densities in  
15 excess of  $10^6$  A/cm<sup>2</sup> at 77 degrees K. when prepared on lattice-matched substrates.

Referring now to Fig. 3, in order to improve the surface characteristics of the substrate 301 of composite 300, for receiving a superconducting oxide coating 303, a  
20 buffer layer (or multiple buffer layers) 302 is deposited in an epitaxial process onto the cube-textured alloy substrate 301. Any of the deposition processes listed above, among others, can be used for depositing the buffer layer 302. A heat treatment can be included to  
25 form the buffer layer in an epitaxial manner. The buffer layer 302 has a thickness of approximately 0.1 to 10.0 micrometers, and preferably 0.1 to 5.0 micrometers more

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preferably 0.2 to 0.8 micrometers. It includes a single metal or oxide layer, or can be a multiple layered structure. A structure in which the buffer layer has two layers is shown in Fig. 3A where the substrate 301 is  
5 covered with a layer 304 and subsequently a second layer 305, where the combination of layers 304 and 305 form the buffer layer. The multiple layers 304 and 305 can include any combination of layers, such as a metal layer 304 with an oxide layer 305 on top, or an oxide layer 304  
10 with another oxide layer 305 on top. Alternatively, referring to Fig. 3B, the buffer layer can include three or even more layers. In this arrangement, the substrate 301 is coated with a metal or oxide layer 306 which in turn is coated with additional metal or oxide layers 307  
15 and 308 before deposition of the superconducting layer 303.

Referring to Figs. 3, 3A and 3B, a top layer 310 comprising a noble metal (such as silver, gold, palladium, platinum, rhodium, iridium, rhenium or alloys  
20 thereof) is optionally deposited on the superconducting layer 303. This layer 310 prevents environmental degradation of the superconducting layer, and provides an alternative current path if the superconducting layer is locally degraded and unable to fully carry the  
25 superconducting current. Also, layer 310 provides an additional site to solder the conductor.

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The metals for the top and buffer layers are typically noble metals or noble metal alloys. By "noble metal" is meant a metal whose reaction products are thermodynamically stable under the reaction conditions employed relative to the desired superconducting ceramic, and/or a metal which does not react with the superconducting ceramic or its precursors under the conditions of manufacture of the composite. The noble metal can be a metal different from metallic matrix elements of the desired superconducting ceramic. The noble metal can be silver or a silver/gold alloy, but it can also be a stoichiometric excess of one of the metallic elements of the desired superconducting ceramic, such as yttrium. Silver (Ag) and silver alloys are the most preferred noble metals. Other noble metals include platinum, gold, palladium, rhodium, iridium, ruthenium, rhenium or alloys thereof. The oxides that are used for the buffer layers are typically stable oxides with a cubic structure such as MgO, cubic  $\text{Al}_2\text{O}_3$ , yttria, YSZ, or rare earth oxides such as  $\text{CeO}_2$ ,  $\text{Yb}_2\text{O}_3$ , etc. or mixtures of these oxides.

By coating the entire substrate, front, back, and/or the sides, with a buffer layer before the deposition of the superconducting layer, the oxidation resistance of the substrate is improved. Fig. 3 shows a substrate with this optional buffer layer 309 on the bottom side of the substrate.

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Referring to Fig. 4, there is shown a partial cross-section of a superconducting composite 400. In this embodiment, the composite 400 has a substrate 401 with a pair of surfaces that are each coated with a  
5 buffer layer 402. A superconducting oxide 403 is coated on each of the buffer layers 402. In an alternate arrangement, as shown in Fig. 5, the composite 500 has a substrate 501 which is fully surrounded by a buffer layer 502. Furthermore, a superconducting oxide layer 503  
10 fully coats the buffer layers 502 on all surfaces of the composite 500.

Referring to Fig. 6, there is shown a partial cross section of a superconducting composite 600. In this embodiment, the composite 600 has a substrate 601  
15 with a pair of surfaces that are each coated with a buffer layer 602. A superconducting oxide 606 is then coated on one side of buffer layer 602. A second buffer layer 603 is coated onto layer 606, after which a second superconducting oxide layer 607 is deposited on this  
20 buffer layer 603. In this manner, a multi-layered structure can be built which, for example, has four superconducting layers (606, 607, 608 and 609) interspersed with three substrate layers (603, 604, and 605). This multiple structure increases the current  
25 carrying capability of the conductor. In this example, the top superconducting layer 609 is coated with a noble metal layer 610 for environmental protection of the

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superconductor 609, an alternate current path, and additional sites to solder the conductor.

#### EXAMPLE 1

A cube-textured copper-nickel alloy according to  
5 the present invention is produced according to the following method. 99.999% pure Ni and Cu pieces (pellets mixed with coarse powders) are weighed in a ratio of 68 at% Cu and 32 at% Ni. The pieces are mixed and loaded in a water cooled copper hearth of an arc melter which  
10 operates in a protective atmosphere. The Cu+Ni mixture is melted and solidified several times, to ensure adequate mixing, at a temperature well above the melting temperatures for several minutes. The solidified and cooled alloy is mechanically formed in the shape of a  
15 solid cylinder, and is rolled, using 10% deformation per pass, to a total reduction of 99% without any intermediate stress anneal process. The resulting tape is heat treated at 850°C for 4 hrs using a protective gas of 95% argon and 5% hydrogen. This tape shows mainly a  
20 single, bi-axial cube texture, with a minor twinning element which can be seen in the (111) pole figure of Fig. 8.

#### EXAMPLE 2

A 32 mm diameter oxygen free copper can is loaded  
25 with a mixture of Cu and Ni pieces, and the overall exact

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stoichiometry (including the weight of the copper can) is further adjusted with Cu powder, to a mixture of 16 at% Ni, 84 at% Cu. This can is placed inside a 38 mm diameter thin-walled alumina crucible and heated in a protective atmosphere using a induction melter at about 1170°C, for up to 5 minutes. The use of the induction melter and the fact that the alumina is not an electrical conductor causes stirring in the melt, which promotes homogenization. After solidification, the alloy is removed from the crucible. To enhance homogeneity, the cast is remelted using a similar crucible and the same induction melter, again under vacuum and at the same conditions. The cast alloy, which has a cylindrical shape, is machined to a diameter of 31 mm and extruded to a 17 mm diameter bar. This bar is homogenized at 950°C for 24 hrs. It is machined to a 16 mm diameter billet, suitable for hydrostatic extrusion. It is extruded to a 3 mm diameter wire and subsequently rolled using a reversible direction rolling technique, with a four-high rolling mill at a rolling speed of 6 m/min, and reduction per pass of 10%. The total reduction in thickness is 98.9%. Subsequently, it is heat treated at 850°C for 4 hrs under a 95% argon - 5% hydrogen gas mixture. This tape has a single bi-axial cube texture and a FWHM value of 6°. A (111) pole figure is shown of this alloy in Fig. 7. The pole figure demonstrates a single, high quality cube texture.



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EXAMPLE 3

A similar process is followed as in Example 2, but the mixture is 26.5 at% Ni and 73.5 at % Cu. The alloy was extruded to a tape, which was rolled to a reduction in thickness of 96%. The tape was heat treated for 4 hours at 850 degrees Celsius. The final tape made with this alloy has a single bi-axial cube texture, with a FWHM value of 12°. A (111) pole figure of this alloy is shown in Fig. 9.

10

EXAMPLE 4

A similar process is followed as in Example 2, but now the mixture is 37 at% Ni and 63 at % Cu. The final foil made with this alloy again has a single bi-axial (100)[001] cube texture, with a FWHM value of 10°. A (111) pole figure of this alloy is shown in Fig. 10.

It will be obvious to those skilled in the art that various changes and modifications can be made therein without departing from the scope of the invention as defined by the appended claims.

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What is claimed is:

1. A cube-textured alloy comprising 5 to 45 atomic percent nickel and the balance being copper.

5        2. A superconducting composite comprising,  
a cube-textured alloy substrate formed from an alloy with 5 to 45 atomic percent nickel and the balance being copper, and  
a superconducting oxide coating said cube-textured alloy substrate on at least one surface.

10       3. The superconducting composite of claim 2 wherein the superconducting oxide is a rare earth superconducting copper oxide.

4. The superconducting composite of claim 2 wherein the superconducting oxide is one of the yttrium-  
15 barium-copper-oxide superconducting phases.

5. The superconducting composite of claim 2 wherein said superconducting oxide coating has a thickness of approximately 1 micrometer to 20 micrometers.

20       6. A superconducting composite comprising,  
a cube-textured alloy substrate comprising an alloy of 5 to 45 atomic percent nickel with the balance being copper,  
a buffer layer coated on said substrate, and  
25 a superconducting oxide coated on said buffer layer.

7. The superconducting composite of claim 6 wherein the superconducting oxide is a rare earth

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superconducting copper oxide, a yttrium-barium-copper superconducting oxide or mixtures thereof.

8. The superconducting composite of claim 7 wherein the superconducting oxide is one of the yttrium-barium-copper-oxide superconducting phases.

9. The superconducting composite of claim 6 wherein said superconducting oxide coating has a thickness of approximately 1 micrometer to 20 micrometers.

10 10. The superconducting composite of claim 6 wherein said buffer layer has a thickness of approximately 0.1 micrometer to 10 micrometers.

11. The superconducting composite of claim 6 wherein said buffer layer comprises metals, alloys, oxides, or combinations thereof.

12. A process for forming a cube-textured alloy comprising the steps of:  
creating a mixture of 5 to 45 atomic percent nickel and the balance being copper;  
20 melting said mixture into a single phase liquid;  
solidifying a copper-nickel alloy from said single phase liquid;  
deforming said alloy;  
planar deforming said alloy; and  
25 heat treating said alloy to form a bi-axially textured alloy with a cube texture.

13. The process of claim 12 further comprising the step of homogenizing said alloy with a heat treatment

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after said deforming step and before said planar deforming step.

14. The process of claim 12 wherein said planar deforming step is performed at room temperature.

5 15. The process of claim 12 wherein said planar deforming step is performed between -200 and +600°C.

16. The process of claim 12 further comprising the step of deforming said alloy in an axially symmetric manner after said deforming step, and before said planar  
10 deforming step.

17. A process for forming a superconducting composite comprising the steps of:

forming a cube-textured alloy substrate from an alloy of 5 to 45 atomic percent nickel and the balance  
15 being copper, said substrate having at least one surface;  
coating said at least one surface of said substrate with a superconducting oxide.

18. The process of claim 17 wherein said superconducting oxide is a rare earth superconducting  
20 copper oxide, a yttrium-barium-copper superconducting oxide or mixtures thereof.

19. The process of claim 18 wherein said superconducting oxide is one of the yttrium-barium-copper-oxide superconducting phases.

25 20. The process of claim 17 wherein said superconducting oxide coating has a thickness of approximately 1 micrometer to 20 micrometers.

- 25 -

21. A process for forming a superconducting composite comprising the steps of:

forming a cube-textured alloy substrate from an alloy of 5 to 45 atomic percent nickel and the balance  
5 being copper;  
depositing a buffer layer on said substrate;  
depositing a superconducting oxide on said buffer layer.

22. The process of claim 21 wherein said  
10 superconducting oxide is a rare earth superconducting copper oxide, a yttrium-barium-copper superconducting oxide or mixtures thereof.

23. The process of claim 22 wherein said superconducting oxide is one of the yttrium-barium-  
15 copper-oxide superconducting phases.

24. The process of claim 21 wherein said superconducting oxide coating has a thickness of approximately 1 micrometer to 20 micrometers.

25. The process of claim 21 wherein said buffer  
20 layer has a thickness of approximately 0.1 micrometer to 210 micrometers.

26. The process of claim 21 wherein said buffer layer comprises metals, alloys, oxides, or combinations thereof.

100	
101	SELECT AND WEIGH THE CONSTITUENT METALS
102	MELT THE CONSTITUENTS AND COOL
103	REMELT TO ENHANCE HOMOGENEITY
104	SHAPE THE SOLIDIFIED MELT AND REDUCE IN SIZE TO FURTHER HOMOGENIZE
105	MECHANICALLY DEFORM THE SHAPE TO A SMALLER SIZE AND RECRYSTALLIZE TO FORM A SMALL GRAIN SIZE
106	DEFORMING THE SHAPE IN AN AXIALLY SYMMETRIC MANNER TO A SMALLER SIZE.
107	PLANAR DEFORM THE ALLOY TO A REDUCTION IN THICKNESS OF BETWEEN 85% TO 99.9%
108	HEAT TREAT AT A TEMPERATURE EXCEEDING 250°C BUT NOT MORE THAN 95% OF THE MELTING TEMPERATURE

FIG. 1

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FIG. 2

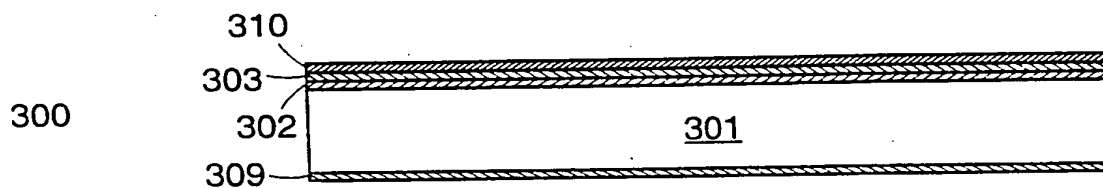


FIG. 3

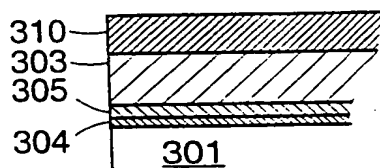


FIG. 3A

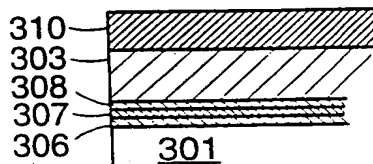


FIG. 3B

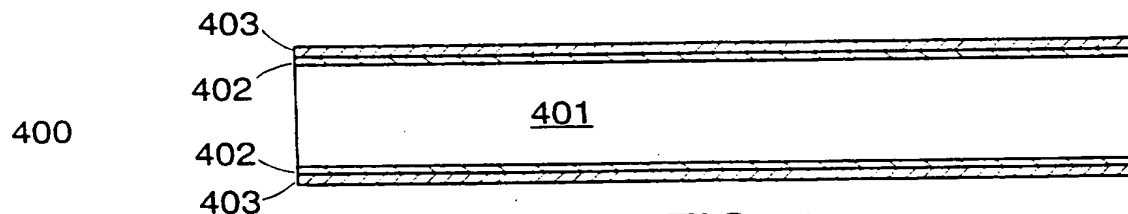


FIG. 4

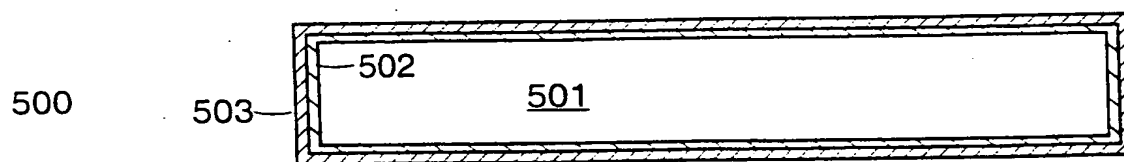


FIG. 5

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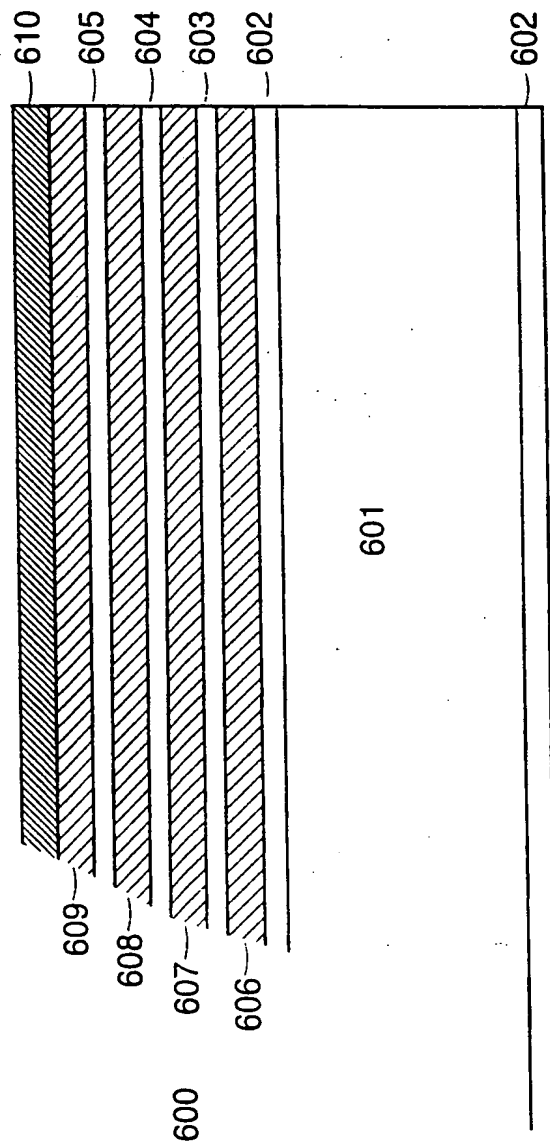


FIG. 6



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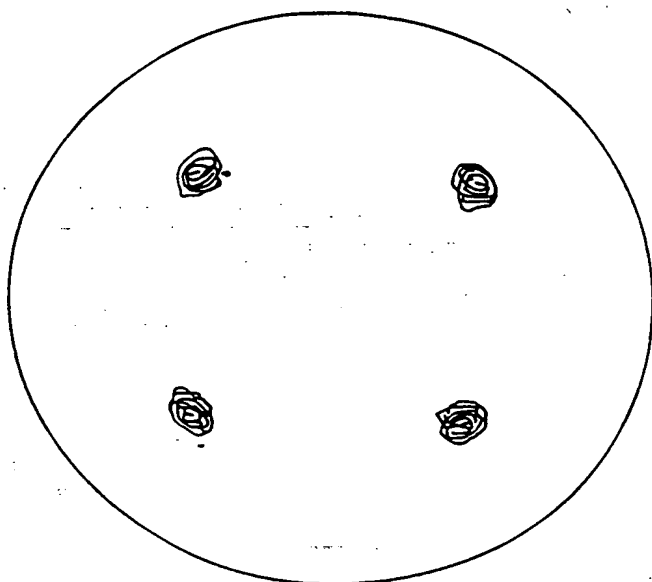


FIG. 7

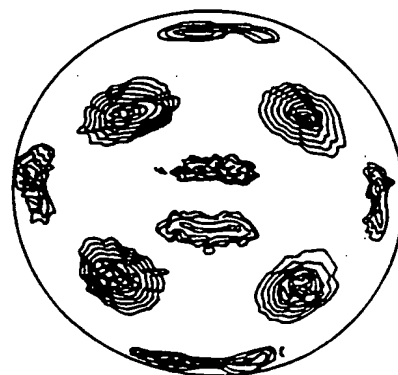


FIG. 8

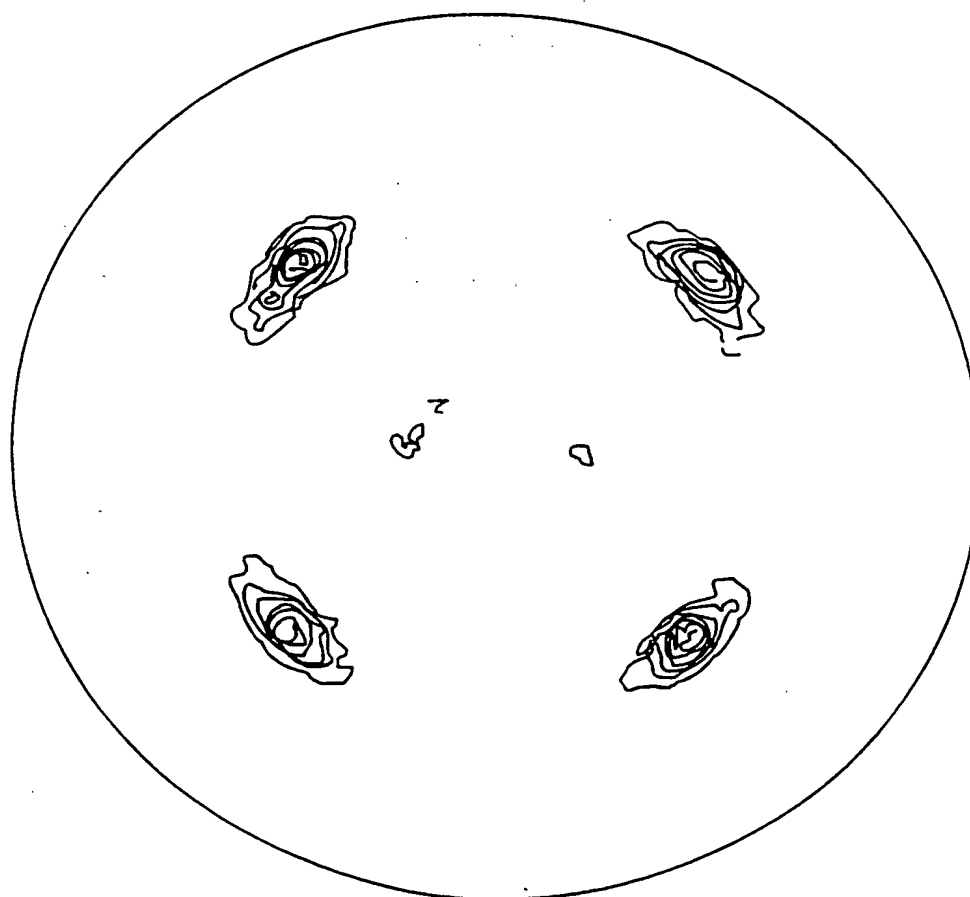


FIG. 9

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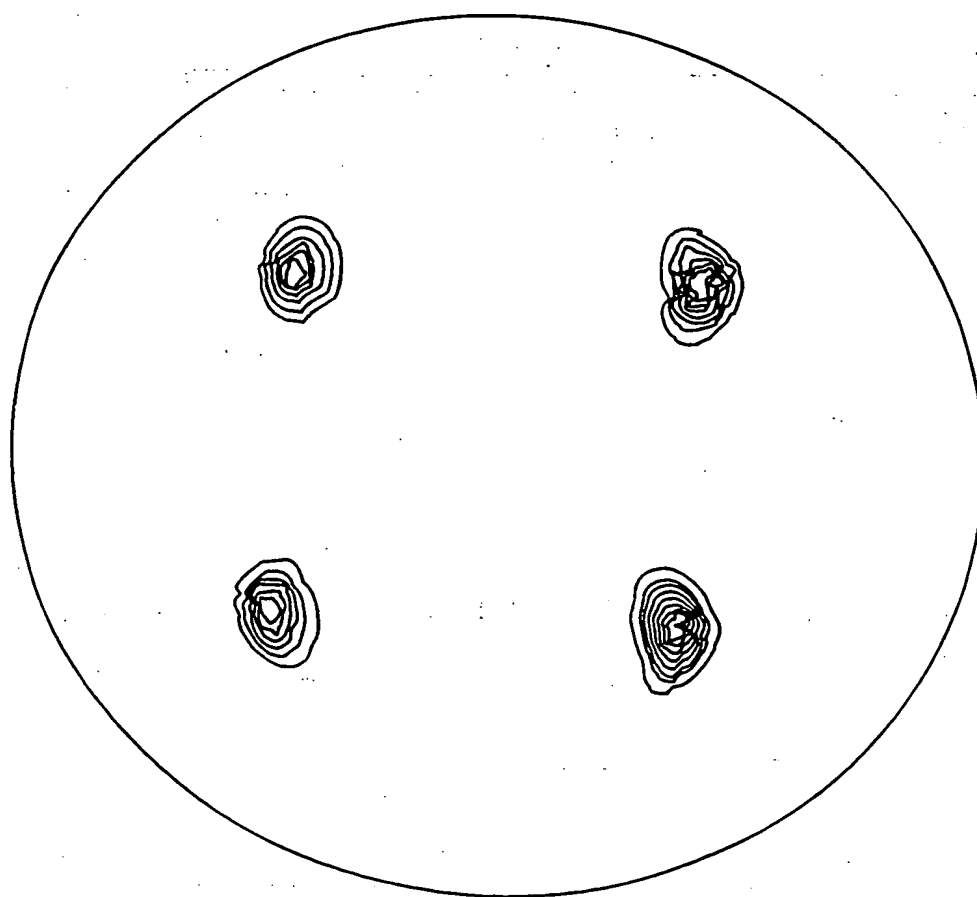


FIG. 10

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/20407

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C30B 29/22; C22F 1/00; B05D 15/04, 31/26

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 505/473, 236, 474, 470, 500; 117/94, 95, 101, 106; 148/435; 420/485

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, CAS ONLINE

search terms: superconduct, alloy, nickel, copper

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,439,877 A (FACE) 08 August 1995.	1
A	US 5,006,507 A(WOOLF et al) 09 April 1991.	1
A	US 4,927,788 A(NAKASHIMA et al) 22 May 1990.	1
A	US 5,516,484 A (KUBOSONO et al) 14 May 1996.	1
Y	US 4,578,320 A (MAHULIKAR et al) 25 March 1986, col. 2 line 20-40.	1-26
Y	WO 96/32201 A1( GOYAL et al) 17 October 1996, note examples.	1-26

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search

27 JANUARY 1999

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

International application No. ---  
PCT/US98/20407

## A. CLASSIFICATION OF SUBJECT MATTER: US CL :

505/473, 236, 474, 470, 500; 117/94, 95, 101, 106 ; 148/435 ; 420/485



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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**08/942,038**      **1 October 1997 (01.10.97)**      **US**(71) Applicants: **AMERICAN SUPERCONDUCTOR CORPORATION [US/US]; Two Technology Way, Westborough, MA 01581 (US). THE REGENTS OF THE UNIVERSITY OF CALIFORNIA [US/US]; 21st floor, 300 Lakeside Drive, Oakland, CA 94612-3550 (US).**(72) Inventors: **FRITZEMEIER, Leslie, G.; 72 Concord Road, Acton, MA 01720 (US). THOMPSON, Elliott, D.; 157 Rathbun Street, Coventry, RI 02816 (US). SIEGAL, Edward, J.; 28 Magnolia Street, Malden, MA 02148 (US). THIEME, Cornelis, Leo, Hans; 21 Mill Road, Westborough, MA 01581 (US). CAMERON, Robert, D.; 90 Daniels Street, Franklin, MA 02038 (US). SMITH, James, L.; 320 Donna Avenue, Los Alamos, NM 87544 (US). HULTS, W., Larry; 811 Tiffany Court, Los Alamos, NM 87544 (US).**(74) Agent: **WALPERT, Gary, A.; Fish & Richardson P.C., 225 Franklin Street, Boston, MA 02110-2804 (US).**(81) Designated States: **AU, CA, CN, JP, NZ, RU, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).****Published***With international search report.  
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*(54) Title: **SUBSTRATES FOR SUPERCONDUCTORS**

100	
101	SELECT AND WEIGH THE CONSTITUENT METALS
102	MELT THE CONSTITUENTS AND COOL
103	REMELT TO ENHANCE HOMOGENEITY
104	SHAPE THE SOLIDIFIED MELT AND REDUCE IN SIZE TO FURTHER HOMOGENIZE
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108	HEAT TREAT AT A TEMPERATURE EXCEEDING 250°C BUT NOT MORE THAN 85% OF THE MELTING TEMPERATURE

## (57) Abstract

An alloy capable of forming a (100) [001] cube-texture by thermo-mechanical techniques has 5-45 atomic percent nickel with the balance being copper. The alloy is useful as a conductive substrate for superconducting composites where the substrate is coated with a superconducting oxide. A buffer layer can optionally be coated on the substrate to enhance deposition of the superconducting oxide. The method for producing the alloy can include weighing the metal (101), melting and cooling the constituents (102). The alloy can include melted (103) and shaped (104). The alloy can then be mechanically deformed to a smaller size and recrystallize (105) then deformed in an axially manner (106) and planar deformation (107). The final step is heat treated (108).

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